Substrate Temperature Effects on Structural Optical and Electrical Properties of Vacuum Evaporated Cu_2ZnSnS_4 Thin Films

M. Ben Rabeh*[1], R. Touatti[2], M. Kanzari[3]

[1,2,3]Laboratoire de Photovoltaïque et Matériaux Semi-conducteurs LPMS-ENIT
Département de Génie Insustriel BP 37 Le Belvédère 1002 Tunis Tunisie

*[1]mohamedbenrabeh@yahoo.fr; [2]Rim.touatti@gmail.com; [3]mounir.kanzari@ipeit.rnu.tn

Abstract

The horizontal Bridgman method has been used to synthesize single crystal and near stoichiometric Cu_2ZnSnS_4 compound from elemental Cu, Zn, Sn and S materials and Cu_2ZnSnS_4 thin films were deposited on glass substrates by thermal evaporation method at different substrate temperature in the range of RT to 200°C. X-ray diffraction (XRD) results suggest that CZTS powder crystallized into kesterite structure with a high degree of crystallinity. All thin films are amorphous in structure at lower substrate temperature, while crystalline CZTS films are obtained at higher temperature. Cu_2ZnSnS_4 crystal exhibit p-type conductivity at the surface and are intrinsic in the volume. By cons, all the CZTS thin films are p-type conductivity with resistivity in the range 100-300 Ω.cm. It is noted that increasing substrate temperature Ts from RT to 200°C has reduced resistivity of CZTS thin films.

Keywords

CZTS; Bridgman Method; Tin Films; Vacuum Evaporation

Introduction

The availability and expensiveness of the indium that is used in chalcopyrite-based thin film solar cells lead to the high production costs of the current large-scale thin film solar cells. Therefore, CZTS has been studied as a novel absorber material in order to lower the production cost of solar cell devices. Cu_2ZnSnS_4 compound is an important $AI_2BIICIVX_4$ quaternary semiconductor material, where A=Cu; B=Zn, Cd, Fe, Mn, Ni; C=Si, Ge, Sn and X= S, Se. CZTS exhibiting the kesterite structure with preferential orientation along the [112] direction is derived by replacing the half of indium (In) atoms with zinc (Zn) atoms and the other half with tin (Sn) atoms in the chalcopyrite-type lattice of CIS. It is known that CZTS is one of the potential photovoltaic materials for use as low-cost thin films solar cells, having an optical band gap of 1.5 eV and an absorption coefficient > $10^4 cm^{-1}$ [K. Ito, 1988].

Several research groups have reported the fabrication of CZTS crystals by using iodine vapor transport method [R. Nitsche, 1967; K. Hönes, 2009], the one-pot synthesis of colloidal nanoparticles [Ch. Chory, 2009,2010] and modified Bridgman method [S. Levcenko, 2009]. Other research groups have reported the elaboration of CZTS thin films using thermal evaporation of the elements and binary chalcogenides [Th.M. Friedlmeier, 1997], spray method [H. Yoo, 2011; N. Kamoun, 2007], sulfurization of precursors [H. Katagiri, 2008], rf sputtering [H. Yoo, 2011; J. Seol, 2003], hybrid sputtering [T. Tanaka, 2005], co-evaporation [T. Tanaka, 2006], pulsed laser deposition (PLD) method [S.M. Pawar, 2010; K. Moriya, 2007, 2008], photochemical deposition [K. Moriya, 2005], electrodeposition [X. Zhang, 2008; J.J. Scragg 2008], and electroplating techniques [A. Ennaoui, 2009]. In this study, CZTS was synthesized using simple horizontal Bridgman method in order to prepare a solid bulk compound CZTS target material for physical vapor deposition. It is expected In the near future that the synthesized powders could also be used as a starting powder to prepare CZTS thin films by utilizing vacuum thermal evaporation technique. However, neither a structural characterizations nor optical properties of the mono-source thermal evaporated CZTS thin films have been reported in the literature.

Experimental Methods

Synthesis

The horizontal Bridgman method is described in Ref. [M. Ben Rabeh, 2010]. Briefly, Cu, Zn, Sn and S with a nominal purity of at least 99.999% are mixed together to prepare Cu_2ZnSnS_4 crystal. The mixture was

introduced in an evacuated and sealed quartz tube under a vacuum of 10^{-6} Torr. The tube was inserted into the furnace where the temperature was raised to 1000°C and maintained at this temperature during 48 hours. After homogenization of the melts, the tube was cooled. The obtained crystal was black color with length of 20mm. Crushed powder of this ingot was used as raw material for the thermal evaporation to obtain Cu_2ZnSnS_4 thin films. Fig.1 shows the typical CZTS ingot.

FIG. 1 INGOT OF Cu_2ZnSnS_4 CRYSTAL

Thin Films Growth

Cu_2ZnSnS_4 thin films were prepared by co-evaporation of the CZTS powder in a high vacuum system with a base pressure of 10^{-6} Torr. An open ceramic crucible was used. Thermal evaporation sources were used which can be controlled either by the crucible temperature or by the source powder. The glass substrates were heated at 150°C. Film thickness was measured by interference fringes method [O.S. Heavens, 1950]. Typical as-deposited films thicknesses were 500nm.

XRD

The crystal and samples were characterized with X-ray diffraction at ambient conditions. The data were collected using D8 Advance diffractometer in Bragg Brentano geometry using CuKα = 1.5418Å radiation for the phase identification and crystallographic structure.

Optical Spectrophotometer

The optical transmittance and reflectance of the CZTS thin films was measured with an UV-VIS-NIR spectrophotometer (Shimadzu UV3100F) in the wavelength range of 300-1800nm.

Hot Probe Method

The Hot-Probe method provides a simple yet efficient way to distinguish between n-type and p-type semiconductors using a heated probe and a standard multimeter [B. Van Zeghbroeck, 1997]. The experiment is done by attaching a couple of cold probe and hot probe to a semiconductor surface. Both probes are wired to a sensitive electrometer whose positive terminal is connected to the hot probe and the negative terminal to the cold probe. While the cold and hot probes are applied to an n-type semiconductor, positive voltage readout is obtained in the meter, whereas for a p-type semiconductor, negative voltage is obtained [G. Golan, 2006].

Results and Discussions

Structural Properties

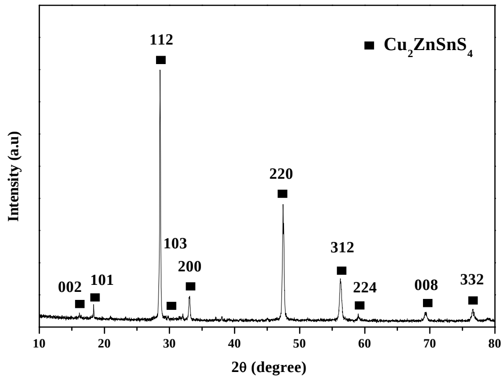

FIG. 2 XRD PATTERN OF Cu_2ZnSnS_4 POWDER

In Fig.2, XRD pattern of the source powder indicates that it is a single phase of Cu_2ZnSnS_4 kesterite structure with tetragonal system but not another phase exists in the structure. This has been verified by JCPDS (Joint Committee on Powder Diffraction Standards) database with card number 26-0575 [JCPDS Card:26-0575]. The main peaks are located at 2θ values of 28.6°, 33.1°, 47.4° and 56.3° with the reflection planes of (112), (200), (220) and (312) respectively. These reflections in XRD pattern are also in good agreement with the reported values [JCPDS Card:26-0575]. The Miller indices h,k,l, the observed and calculated inter-planar spacing (d) and the relative intensities (I/I_0) of the diffraction lines are listed in Table 1. The calculated and observed interplanar spacing are found to be in good agreement with each other. Given the Bragg relation $2d\sin\theta = p\lambda$ and the inter-planar spacing for a tetragonal system $d = (\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2})^{-1/2}$, the lattice constants of the crystals have been determined.

The lattice constants of the a and c axis of the CZTS crystals are $a = 5.412$ Å and $c = 10.848$ Å. These results are in good agreement with these obtained by Nelson Riley [J. B. Nelson, 1945] ($a = 5.407$ Å and $c = 10.815$ Å) and calculated by JCPDS ($a = 5.427$ Å and $c = 10.848$ Å) [JCPDS Card:26-0575]. Fig. 3 shows the results on our XRD measurement of Cu_2ZnSnS_4 thin films prepared at various substrate temperatures in the range of room temperature to 200°C for 2θ scans between 10° and 70°.

TABLE 1 X-RAY PAWDER DIFFRACTION DATA FOR CU_2ZNSNS_4 CRYSTAL

I/I_0 (%)	2θ(°)	d_{hkl}(Å) (Calc)	d_{hkl}(Å) (Obs)	hkl
5	16.283	5.421	5.463	002
9	18.334	4.869	4.875	101
100	28.459	3.126	3.144	112
4	29.861	3.008	2.985	103
11	33.119	2.713	2.703	200
7	37.974	2.368	2.370	211
47	47.399	1.919	1.921	220
18	56.187	1.636	1.635	312
6	59.017	1.565	1.567	224
7	69.286	1.356	1.354	008

It can be found that films deposited at RT, 70 and 150°C were nearly amorphous whereas for higher temperatures, the amorphous background was diminished and diffraction peaks (112) and (200) of CZTS powder were revealed for all samples. The peaks intensity and sharpness rose with increasing substrate temperature. which confirmd that crystallinity of the films were improved with increasing substrate temperature. The size of the crystallites D in the gains can be estimated by the Debye-Scherrer formula [H.P. Klug, 1974]:

$$D = \frac{0.9 \times \lambda}{B \times \cos\theta}$$

Where λ is the X-ray wavelength of 1.5418Å, θ is the Bragg diffraction angle and B is FWHM. The mean grain size of the sample deposited at 70°C, 125°C, 150°C and 200°C is 14 nm, 36 nm, 44 nm and 47 nm, respectively. The grain sizes of the samples increased and FWHM decreased as Ts increasing, implying that the crystallization degree is improved with rising Ts because the rising Ts has improved the mobility of the deposited atoms.

Optical Properties

Figs. 4 and 5 show the reflectance and transmittance spectra of CZTS thin films grown at various temperatures. The optical reflectance of these films varies over the range 20-40% and the transmittance are over 80% in the visible region and the fundamental absorption edges have been clearly observed for all samples. A decrease in transmittance with substrate temperature is observed when Ts is more than 150°C. This decrease in transmittance is due to the increase in crystallinity of films which results in higher scattering of light. The ripples in transmittance and reflectance spectra are attributed to optical interference effects.

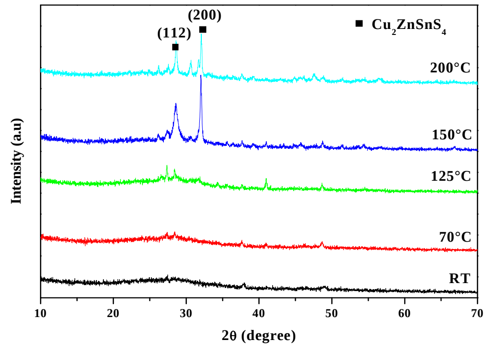

FIG. 3 XRD PATTERNS OF Cu_2ZnSnS_4 THIN FILMS PREPARED AT VARIOUS SUBSTRAE TEMERATURE

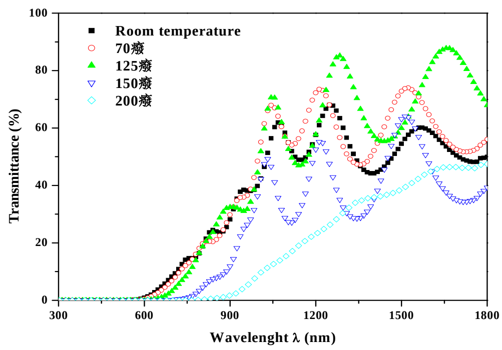

FIG. 4 OPTICAL TRANSMITTANCE OF Cu_2ZnSnS_4 THIN FILMS PREPARED AT VARIOUS SUBSTRAE TEMERATURE

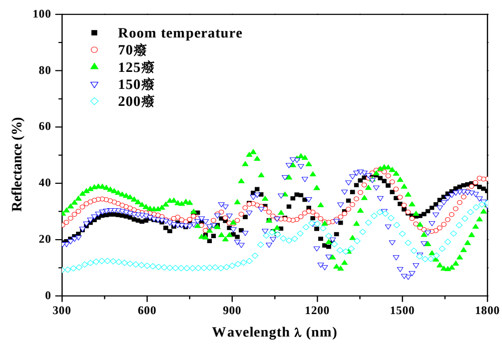

FIG. 5 OPTICAL REFLECTANCE OF Cu_2ZnSnS_4 THIN FILMS PREPARED AT VARIOUS SUBSTRAE TEMERATURE

The fundamental absorption corresponding to the electron excitation from valance band to conduction bad can be used to evaluate the value of the optical band gap. The optical band gap of the film is determined by the application of the Tauc model and the Davis and Mott model in the high absorbance region [J. Tauc, 1974; E.A. David, 1970]:

$$(\alpha h\nu) = A(h\nu - Eg)^q$$

Here, A is a constant, hν is the photon energy, and Eg is the optical band gap. For a direct transition, n=1/2 or 2/3 and the former value is more suitable for CZTS film because it gives the best linear curve in the band-edge region. The absorption coefficient α (hν) of CZTS thin films can be calculated from the following relation [D.E. Milovzorov, 2001]:

$$\alpha = \frac{1}{d}\ln\left[\frac{(1-R)^2}{T}\right]$$

Here T is the transmittance, R is the reflectance and d is the film thickness.

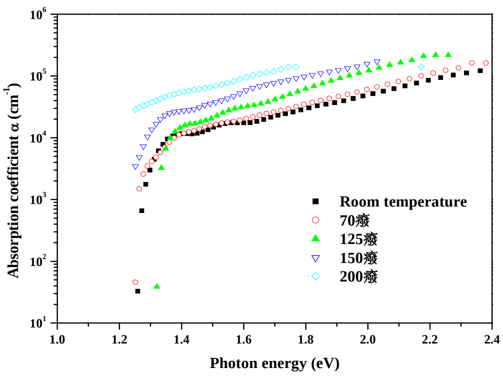

FIG. 6 OPTICAL ABSORPTION COEFFICIENT OF Cu_2ZnSnS_4 THIN FILMS PREPARED AT VARIOUS SUBSTRAE TEMERATURE

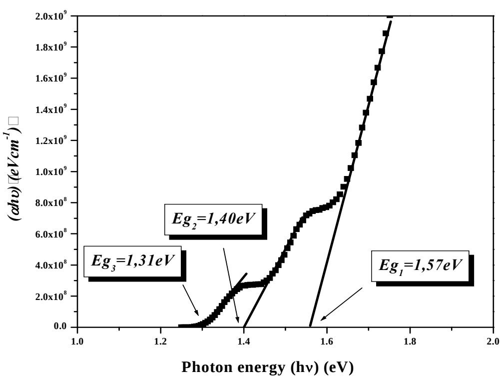

FIG. 7 ENERGY BAND GAPS OF Cu_2ZnSnS_4 THIN FILMS FOR SAMPLES PREPARED AT RT

Fig. 6 shows the absorption coefficients α (hν) versus the photon energy (hν) for CZTS thin films added at various substrate temperatures. It can be seen that all the films have relatively high absorption coefficients between 10^4 cm^{-1} and 10^5 cm^{-1} in the visible and the near-IR spectral range. It is also noted that the absorption coefficient increases with growing substrate temperature. Fig. 7 shows, for the Cu_2ZnSnS_4 thin films deposited at room temperature, the relationship between $(\alpha h\nu)^2$ and hν, and the Eg value obtained by extrapolating the linear portion of the photon energy axis. For the samples prepared at substrate temperature less that 200°C, It is revealed that the existence of three direct gaps Eg_1, Eg_2 and Eg_3 are located at 1.48-1.60 eV, 1.37-1.45 eV and 1.28-1.34 eV, respectively. The existence of three gaps can be explained by the amorphous character of the samples. On the other hand, a single direct gap is obtained at value Eg_1=1.48 eV for samples prepared at substrate temperature of 200°C. The band gap of this film is quite close to the optimum band gap required for a solar cell, indicating that CZTS is very promising material for thin film solar cell applications. The CZTS band gaps at various temperatures have been summarized in Table. 2.

TABLE 2 BAND-GAPS ENERGY, RESISTIVITY AND TYPE OF CONDUCTIVITY OF CU_2ZNSNS_4 THIN FILMS PREPARED AT VARIOUS SUBSTRATE TEMPERATURE

Substrate Temperature (°)	**Band Gaps Energy (eV)**			**Resistivity (Ω.cm)**
	Eg_1	**Eg_2**	**Eg_3**	
RT	1.57	1.40	1.31	325
70	1.52	1.38	1.32	190
125	1.60	1.45	1.34	165
150	1.51	1.37	1.28	143
200	1.48	-	-	90

Electrical Properties

Film resistance was measured between two gold ohmic electrodes previously deposited by thermal evaporation. The type of conductivity of these films was determined by the hot probe method. It was found that the CZTS crystal exhibiting p-type conductivity at the surface is intrinsic in the volume and all the CZTS thin films are p-type conductivity

with resistivity in the range 100-300Ω.cm. It can be seen from Table 2 that these types were in good agreement with those in the literature [T. Tanaka, 2005; J.J. Scragg, 2008].

Conclusions

It has been demonstrated that horizontal Bridgman method was also capable of producing crystal of CZTS and CZTS thin films were deposited by thermal evaporation at various substrate temperatures in the range of RT to 200°C. X-rays of powder analysis showed that only homogenous Cu_2ZnSnS_4 phase was present in the ingot and X-rays of thin films showed that the crystallinity improved and grain size became larger with increasing substrate temperature. CZTS films prepared at 200°C have a band gap of 1.48 eV. In addition, hot probe method indicated that all CZTS samples exhibit p-type conductivity.

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Dr M. Ben Rabeh, Laboratoire de Photovoltaïque et Matériaux Semi-conducteurs, Ecole Nationale d'Ingénieurs de Tunis, Tunis, Tunisie. The field of scientific interest : Materials science, semiconductors, thin films.

Professor M. Kanzari, Laboratoire de Photovoltaïque et Matériaux Semi-conducteurs, Ecole Nationale d'Ingénieurs de Tunis, Tunis, Tunisie. The field of scientific interest : Matérials science, semiconductors, thin films, photonics.